

Property changes of wood-fiber/HDPE composites colored by iron oxide pigments after accelerated UV weathering

ZHANG Zheng-ming • Du Hua • WANG Wei-hong • WANG Qing-wen

Received: 2009-05-30; Accepted: 2009-06-22

© Northeast Forestry University and Springer-Verlag Berlin Heidelberg 2010

Abstract: Four kinds of iron oxide pigments were added into wood-fiber/high-density-polyethylene composites (WF/HDPE) at three different concentrations, to determine the effects of pigments on the changes in the color and mechanical properties of the composites before and after UV accelerated weathering. HDPE, wood fibers, pigments and other processing additives were dry-mixed in a high-speed mixer. The mixtures were extruded by two-step extrusion process with a self-designed twin-screw/single-screw extruder system. Color of the samples was determined according to CIE 1976 $L^*a^*b^*$ system by a spectrophotometer and the bending properties were tested to evaluate the mechanical properties before and after accelerated UV weathering. The result shows that the modulus of elasticity of WF/HDPE did not obviously changed after incorporating with the pigments, but the bending strength increased. After accelerated aging for 2000 h, both color and mechanical properties significantly changed. Iron oxide red and black performed better than the other two pigments, and the pigments dosage of 2.28% in the composites is favourable.

Keywords: wood-plastic composite; pigments; weathering; color; flexural property

Introduction

The use of wood fibers as fillers and reinforcer in thermoplastic industry has gained much acceptance and the resulted wood-plastic composites (WPC) grew rapidly during the past

decade (Markarian 2005). The environmental friendly, uniquely aesthetic and low maintenance characteristics of WPC are driving the fast growth in wood replacement applications.

The global wood thermoplastic composite market was 771 million kilogram in 2003, 85% of which was shared by North America. It is predicted that its local market will continue to experience double-digit growth from 2003 to 2010 (Clemons 2002; Markarian 2005; Ashori 2008). Although WPC was promoted as a low-maintenance and high-durability product, its durability has been a concern. It was shown that WPC exposed to accelerated weathering experienced a color change and a loss in mechanical properties (Clemons 2002; Wechsler et al. 2007). Photostabilizers were used in some studies to protect WPC from color change and photodegradation (Muasher et al. 2006; Stark et al. 2006). The main objective of the present study was to determine the effects of pigments on the changes in the color and mechanical properties of the composites before and after UV accelerated weathering.

Materials and composites preparation

Wood fiber (WF), size between 40–80 mesh, was supplied by local market. High-density polyethylene (HDPE, Type 5000s) and Semi-refined paraffin wax (wax, Type 23998-9011) were supplied by PetroChina. Polyethylene wax (PE wax) was used as dispersion agent of pigments. Coupling agent maleic anhydride grafted polyethylene (MAPE, Type CMG9804) was supplied by Shanghai Sunny New Technology Development Co., LTD. Four kinds of iron oxide pigments were chosen for this study because of their widely application in plastic industry in China. Iron oxide red (Type 120EDS), iron oxide yellow (Type TSY-1H), iron oxide blue (Type KGBL-886) and iron oxide black (Type CB-760) were all supplied by Deqing Toda Sanfeng Pigment.

WF, HDPE, pigments and the additives were used at the level listed in Table 1. Compounding was accomplished by using a self-designed twin-screw (30mm)/single-screw (45mm) extruder system. WF/HDPE composites with or without colorant were extruded. The lumbers with rectangular cross section of

Foundation project: This study was supported by the National Natural Science Foundation of China (30671644, 30771680)

The online version is available at <http://www.springerlink.com>

ZHANG Zheng-ming • Du Hua • WANG Wei-hong •

WANG Qing-wen (✉)

Key Laboratory of Bio-based Material Science and Engineering (Ministry of Education), Northeast Forestry University, Harbin 150040, P.R.China. E-mail: qwwang@nefu.edu.cn

Responsible editor: Chai Ruihai

40mm×4mm were then cut into small samples.

Testing and analysis

Accelerated UV weathering was conducted in a QUV

weatherometer (Q-panel, US). According to the standard method of ASTM G154 (2000), the weathering schedule involved 8h UV irradiation at 60°C and 4 h condensation at 50°C. The average irradiance was 0.77W/m² at 340 nm wave length. The total weathering time is 2000 h.

Table 1. WF/HDPE composites preparation design and ingredient levels (phr)

Formulation	HDPE	WF	MAPE	wax	PE wax	Red	Yellow	Blue	Black	Pigment content, %
control	100	150	5	1.25	1.25	0	0	0	0	0
1	100	150	5	1.25	1.25	2	0	0	0	0.77
2	100	150	5	1.25	1.25	4	0	0	0	1.53
3	100	150	5	1.25	1.25	6	0	0	0	2.28
4	100	150	5	1.25	1.25	0	2	0	0	0.77
5	100	150	5	1.25	1.25	0	4	0	0	1.53
6	100	150	5	1.25	1.25	0	6	0	0	2.28
7	100	150	5	1.25	1.25	0	0	2	0	0.77
8	100	150	5	1.25	1.25	0	0	4	0	1.53
9	100	150	5	1.25	1.25	0	0	6	0	2.28
10	100	150	5	1.25	1.25	0	0	0	2	0.77
11	100	150	5	1.25	1.25	0	0	0	4	1.53
12	100	150	5	1.25	1.25	0	0	0	6	2.28

A spectrophotometer Mold NF333 was used to measure the color of weathered and un-weathered samples according to the CIE 1976 L^{*}a^{*}b^{*} color system. An increase in L^{*} means the samples is lightening. The color coordinates a^{*} and b^{*} range from -150 to +150. They are defined as the red/green coordinate, a^{*} (+Δa^{*} signifies a color shift toward red, -Δa^{*} toward green) and the yellow/blue coordinate, b^{*} (+Δb^{*} toward yellow, -Δb^{*} toward blue). The total color change ΔE^{*} was calculated according to ASTM D2244 (2004) as seen in the following equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

Where ΔL^{*}, Δa^{*} and Δb^{*} are the difference of initial (before weathering) and final (after weathering) values of L^{*}, a^{*} and b^{*}.

The flexural properties of the composites, bending strength (BS) and modulus of elasticity (MOE), were tested by using a Universal Mechanical Tester (Reger Instrument) according to ASTM D790 (2003). The size of tested samples was 80mm×13mm×4mm. 7 specimens were repeated.

To characterize the surface-texture changes, the surfaces of

weathered samples and control samples were sputter-coated with gold and then analyzed using a scanning electron microscope (FEI QUANTA 2000).

Results and discussion

Effects of accelerated weathering on the color of EF/HDPE composites

Changes in Lightness (L^{*}) and color coordinates (a^{*} and b^{*}) of the samples after exposed to 2000h UV weathering were presented in Table 2. The Data indicated that, all the samples were bleached after weathering. As expected, the control sample without any pigment discolored most seriously, its L^{*} value changed from 42.2 to 85.4 (ΔL^{*} 43.18), increased 102%. A thin layer of white exudates was observed covering the surface of the weathered control sample. This may be mainly due to the incorporation of wood fibers into HDPE matrix, which had a deleterious effect on the ability of the matrix to resist exposure to UV radiation (Matuana et al. 2001).

Table 2. Discoloration of WF/HDPE composites after 2000h UV weathering

Pigment content%	Red			Yellow			Blue			Black		
	ΔL [*]	Δa [*]	Δb [*]	ΔL [*]	Δa [*]	Δb [*]	ΔL [*]	Δa [*]	Δb [*]	ΔL [*]	Δa [*]	Δb [*]
0.77	20.41	4.19	-0.31	26.01	-3.47	8.75	38.24	-8.32	-14.72	23.61	1.73	0.12
1.53	14.82	2.43	-5.27	21.50	-2.37	9.12	32.86	-10.05	-17.44	17.91	1.66	1.62
2.28	10.92	2.63	-0.32	16.99	-2.10	10.34	31.51	-10.56	-18.88	16.31	1.90	2.80
Control:	ΔL [*] 43.18	Δa [*] -6.87	Δb [*] -12.99									

By contrast, all the samples colored by iron oxide pigments did not lighten as much as the unpigmented ones and had no exudates appeared on the surface. The change in lightness, ΔL^{*}, significantly decreased when pigments were added. With the

increase of pigment content, ΔL^{*} value became less and less. When iron oxide pigment was added at a dosage of 2.28%, ΔL^{*} of all colored samples arrived a lower values. The average increasing of L^{*} was 64%, which indicated that colored samples were

bleached much less compared to those uncolored sample which experienced 102 % increase in L^* as mentioned above.

After weathering, the color of samples dyed with iron oxide yellow and iron oxide blue tended to become more yellow and blue, respectively. In other words, with the increase in these two pigments, the samples' color was getting more and more vivid when exposed to UV weathering. Iron oxide black contained some carbon black which is an excellent photostabilizer, and this may contribute to the black samples getting well photostability and the color changed slightly through out the exposure cycle.

The total color change (ΔE^*) of WF/HDPE composites samples after 2000 h UV exposure were shown in Table 3. Similar to the trend of lightness and color coordinate, the control sample got the most obvious color change, $\Delta E^* = 45.6$. However, when pigments were added, the color changes of the samples were less significant than that of the control sample. Influence of pigment content on ΔE^* was also considerable. The more the pigment was added, the less the color of the composite faded. Iron oxide red and black still performed better than the other pigments. This mainly because all the particles of these two pigment were inorganic and had good light stability.

Table 3. ΔE^* of WF/HDPE colored by iron oxide pigments after 2000h UV weathering

Pigment content (%)	Red	Yellow	Blue	Black
0.77	20.84	27.66	41.82	23.67
1.53	15.92	23.47	38.53	18.06
2.28	11.23	20.00	38.22	16.66
Control:	45.61			

Table 4. Flexural properties of WF/HDPE colored by iron oxide pigments before and after 2000-h UV weathering

Pigment Content (%)	Time h	Red		Yellow		Blue		Black	
		BS, MPa	MOE, GPa	BS, MPa	MOE, GPa	BS, MPa	MOE, GPa	BS, MPa	MOE, GPa
0.77	0	46.30	4.23	43.48	4.03	44.06	4.24	55.74	4.07
	2000	35.79	3.15	35.06	3.08	33.10	3.05	44.94	3.59
1.53	0	47.21	4.28	44.41	3.96	43.09	3.92	52.83	4.04
	2000	36.07	3.17	36.11	3.13	24.26	3.00	43.74	3.47
2.28	0	46.52	4.10	44.41	4.04	41.97	4.17	53.99	4.03
	2000	36.96	3.18	35.80	3.14	32.91	2.96	47.84	3.76
Control		0h: MOE 43.11, BS 3.78; 2000h: MOE 33.95, BS 2.88							

The influence of pigments used in this study on the mechanical properties did not appear much differently. After UV weathering, MOE and BS loss of all colored samples was about 1GPa and 10MPa respectively. However, iron oxide black behaved more differently than the other 3 pigments, a bigger strength of the composites before weathering and less MOE/BS loss after weathering were observed. This may due to the reinforcing and photostabilization effects of carbon black in iron oxide black.

Both UV radiation and water condensation may cause the loss in mechanical property. Exposing to UV radiation can change the crystallinity of plastic matrix (Stark et al. 2003; Stark et al. 2004a) and water can swell wood particles. The swelling of the wood particles could cause microcracks in the matrix and reduce the efficiency of stress transfer from wood fiber to plastic matrix,

Iron oxide blue and yellow used in this study contained some organic ingredients as the manufacturer stated but the compounds were not specified. These organic components are easier to degrade when exposed to the UV light. So the WF/HDPE composite samples colored by these two pigments got more color change after weathering.

The lighting or fading of WF/HDPE composites was mainly due to the photodegradation and bleaching of the wood component (Muasher et al. 2006). In addition, the composite also experienced some pigment loss during weathering. Some of the pigments particles at the surface of the composites may flake off when they were exposed to weathering recycle. Although all samples changed their color after 2000h weathering, the samples colored by iron oxide pigments still performed superiorly in reserving color compared to the control sample.

Effects of accelerated weathering on the flexural properties of EF/HDPE composites

Changes in flexural properties of EF/HDPE composites after 2000h accelerated weathering were presented in Table 4. These results showed that MOE and BS of all the samples decreased evidently throughout the weathering cycle. MOE and BS of control sample decreased 21.2% and 23.8% respectively. Similarity to the control samples, most iron oxide pigments didn't appear to aid in the retention of mechanical properties at any pigment content, and the loss of MOE and BS also did not change obviously when the pigment content increased. In some formulations, the mechanical properties even loose more than that of the control sample. For example, the loss of MOE and BS of the red color samples were higher than those of the control sample, no matter how much pigment was contained.

which led to the decrease in MOE and BS. Research showed that the addition of pigments to a composite physically blocked UV radiation and effectively prevented the composite from weathering, the evident loss of the mechanical properties may mainly attribute to water swelling (Stark et al. 2003; Stark et al. 2004b; Stark et al. 2006). Worse interface caused more water swelling and significant mechanical properties loss occurred finally.

Scanning Electron Microscopy

Four representative SEM images of the composites surface were taken to analyze the effects of the UV accelerated weathering on the surface condition of the control and the colored WF/HDPE composites (Fig.1). As we know, there is a thin layer of polymer

film formed on the surface of WPC during extrusion. All un-weathered WF/HDPE composites samples, control and colored by iron oxide pigments, presented smooth surface morphology under SEM. However, after 2000 h of accelerated UV irradiation and dewing, significant cracks occurred on the surface of control sample without any pigment in it, and many tiny flakes were exfoliated from the sample surface. It can be seen in Fig.1 that the colored samples were well protected by adding pigments and appeared smoother than exposed control sample, and that better protection effect was found at higher pigment dosage of 2.28%. However, a lot of surface cracks still occurred after 2000h weathering and some wood fibers rose from the surface of the colored WF/HDPE composites samples.

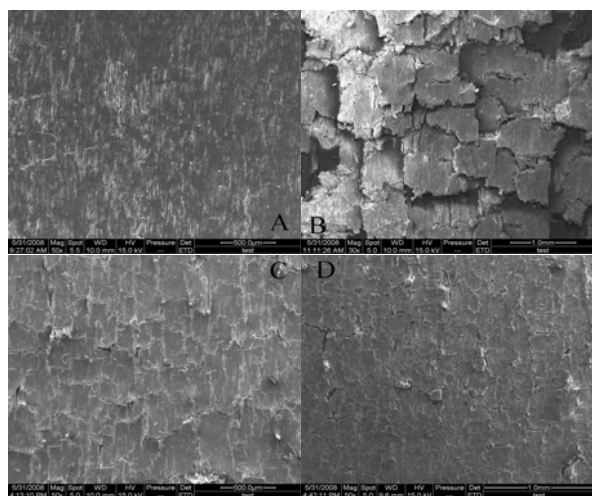


Fig.1 SEM image of samples: (A) control, (B) exposed control, (C) exposed formulation 1, (D) exposed formulation 3

Conclusions

From this investigation, it can be concluded that iron oxide pigments used in this study exhibit a very good performance in protecting WF/HDPE composites from discoloration. Compared with the control, WF/HDPE composites samples colored by iron oxide pigments resulted in less lightening after 2000h exposure to UV radiation and condensation. The changes in lightness decreased with the increasing of pigment dosage, while the color coordinates changed differently for each pigment. However, iron

oxide pigments used in this study didn't appear to aid in maintaining the mechanical properties of the composites, except that iron oxide black containing carbon black exhibited some positive effects on the mechanical properties of the composite.

Iron oxide red and iron oxide black performed better than the other two kinds of iron oxide pigments, and the pigments dosage of 2.28% in the composites is favourable.

References

- Ashori A. 2008. Wood-plastic composites as promising green-composites for automotive industries. *Bioresource Technology*, **99** (11):4661–4667.
- Markarian J. 2005. Wood plastic composites: current trends in materials and processing. *Plastics, Additives and Compounding*, **7**(5): 20–26.
- Clemons CM. 2002. Wood-plastic composites in the United States: the interfacing of two industries. *Forest Prod J*, **52**(6): 10–20.
- Wechsler A, Hiziroglu S. 2007. Some of the properties of wood-plastic composites. *Building and Environment*, **42**: 2637–2644.
- ASTM G154. 2000. Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials.
- ASTM D 2244. 2002. Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates.
- ASTM D790. 2003. Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.
- Matuana LM, Kamdem DP. 2001. Photoaging and stabilization of rigid PVC/Wood-fiber composites. *Journal of Applied Polymer Science*, **80**: 1943–1950.
- Muasher M, Sain M. 2006. The efficacy of photostabilizers on the color change of wood filled plastic composites. *Polymer Degradation and Stability*, **91**: 1156–1165.
- Stark N M, Matuana L M. 2004a. Surface Chemistry Change of Weathered HDPE/Wood-Flour Composites Studied by XPS and FTIR Spectroscopy. *Polymer Degradation and Stability*, **86**: 1–9.
- Stark NM, Matuana LM. 2004b. Surface chemistry and mechanical property changes of wood-flour/high-density- polyethylene composites after accelerated weathering. *Journal of Applied Polymer Science*, **94**: 2263–2273.
- Stark NM, Matuana LM. 2003. Ultraviolet weathering of photostabilized wood-flour filled high-density-polyethylene composites. *Journal of Applied Polymer Science*, **90**: 2609–2617.
- Stark NM, Matuana LM. 2006. Influence of photostabilizers on wood flour-HDPE composites exposed to xenon-arc radiation with and without water spray. *Polymer Degradation and Stability*, **91**: 3048–3056.